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1,4,5,8-Tetrakis(arylamino)anthraquinones: Near Infrared Absorbing Dyes

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ABSTRACT

Condensation of 4,5-dinitrochrysazin (DNCZ) and 5,8-dichloroquinizarin (DCQZ) with arylamines in the presence of boric acid (with or without zinc powder) gives 1,4,5,8-tetrakis(arylamino)anthraquinones. The dyes absorb in the near infrared at about 750–770 nm and colour polybutylene terephthalate film in green hues of very good fastness to light and sublimation.

1 INTRODUCTION

There is current interest in the development of near infrared (IR) absorbing dyes for use in optical information recording media for semi-conductor lasers. The gallium-arsenic (Ga-As) diode laser emits IR light at 780–830 nm and the dyes therefore have to absorb above 700 nm. Recently, some near IR absorbing naphthoquinones, phthalocyanines and nickel-complex dyes have been reported.[1–3] Anthraquinonoid dyes have good brightness and fastness to light and sublimation, properties which are important for use in optical information recording media.

The condensation of 4,5-dinitrochryazin (DNCZ) with arylamines to give bright blue (4-arylamino) to bluish green (1,4-bisarylamino) dyes having good light and sublimation fastness on polyester fabrics has been reported.[4–7] The authors now report the condensation of DNCZ (in the presence of boric acid and zinc powder) and of 5,8-dichloroquinizarin (DCQZ) (in the presence of boric acid and potassium acetate) with excess arylamines to give tetrakis(arylamino)anthraquinones.

2 EXPERIMENTAL

2.1 1,4,5,8-tetrakis(arylamino)anthraquinones (I)

2.1.1 Method A

DNCZ (3·3 g, 0·01 mol), boric acid (1·0 g), zinc powder (0·5 g) and aniline (40 ml) were stirred under reflux for 37·5 h. The liquor was cooled to room temperature and then poured into ethanol (30 m) and left to stand overnight. The precipitate was filtered and washed with 10% hydrochloric (300 ml) and then with water until the washings were neutral and colourless. Recrystallization from 2-methoxyethanol gave 2·74 g (48%) 1,4,5,8-tetrakis(anilino)anthraquinone (dye **I.1**), m.p. 317°C.

Replacing aniline in the above by *p*-ethoxyaniline (10·96 g, 0·08 mol) and refluxing for 30 h gave 3·37 g (45%) 1,4,5,8-tetrakis(4′-ethoxyanilino)-anthraquinone (dye **I.2**), m.p. 379°C.

2.1.2 Method B

A mixture of DCQZ (3·1 g, 0·01 mol), boric acid (1·0 g), potassium acetate (0·5 g) and *p*-ethoxyaniline (35 ml) was stirred under reflux for 14·5 h. The reaction liquor was cooled to room temperature and the product isolated as in Method A above to give, after recrystallization from 2-methoxyethanol, 3·13 g (42%) 1,4,5,8-tetrakis(4′-ethoxyanilino)anthraquinone (dye **I.2**).

Dye **I.1** (2·34 g, 41%) was similarly obtained using aniline and refluxing for 20 h.

TABLE 1
Spectroscopic Data of **I**

Dye	*R*	*Mass (m/e)*	*IR (KBr)*[a]	*^1H NMR*[b] *(acetone-d_6)*		
I.1	H	572(M^+)	3300, 3230 νNHR			
			1610 C=O	6·659	7·361	
			1580, 1500 ar.			
			1300 C—N	6·627	7·351	
			750, 700, 660 ar. C—H b.o.o.p.		7·035	
					6·999	
I.2	*p*-OC_2H_5	748(M^+)	3270, 3230, 3130 νNHR			
			2950–2860 CH_3st.			
			1600 C=O	6·776	6·887	3·996
			1580, 1515, 1480 ar.			1·328
			1380 C_2H_5	6·676	6·849	
			1300, 1250 C—N			
			1190, 1120 ar. C—OH			
			930, 820, 758, 680 ar. C—H b.o.o.p.			

[a] ar., aromatic; b.o.o.p., bending out of plate; st., stretching.
[b] s, singlet; d, doublet.

TABLE 2
Colour and Fastness Properties of I

Dye	*R*	λ_{max}*(log ε) (nm) in chlorobenzene*	*Dyeing on polybutylene terephthalate film*[a]	
			Light fastness	*Sublimation, initial temp.*
I.1	H	400(4·12), 700(4·48) 750(4·50)	6	160°C
I.2	p-OC_2H_5	400(3·19), 725_s(4·47) 770(4·54)	6	160°C

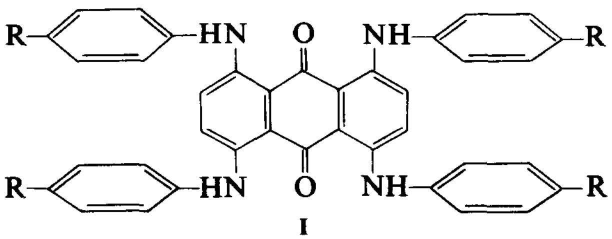
[a] 0·5% o.w.f.

$_s$, Shoulder.

2.2 General

All dyes were purified by TLC on Kieselgel 60 (Merck). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in chlorobenzene at a concentration of 3×10^{-5} g/ml. Characterization data were obtained by mass spectrometry (Hitachi M-52), IR (Hitachi 260-50) and ^{1}H NMR (Varian VxR-300) (Table 1).

Dyeings on polybutylene terephthalate film and evaluation of the light and sublimation fastness were carried out as for related dyes in previous investigations,[8,9] (Table 2).



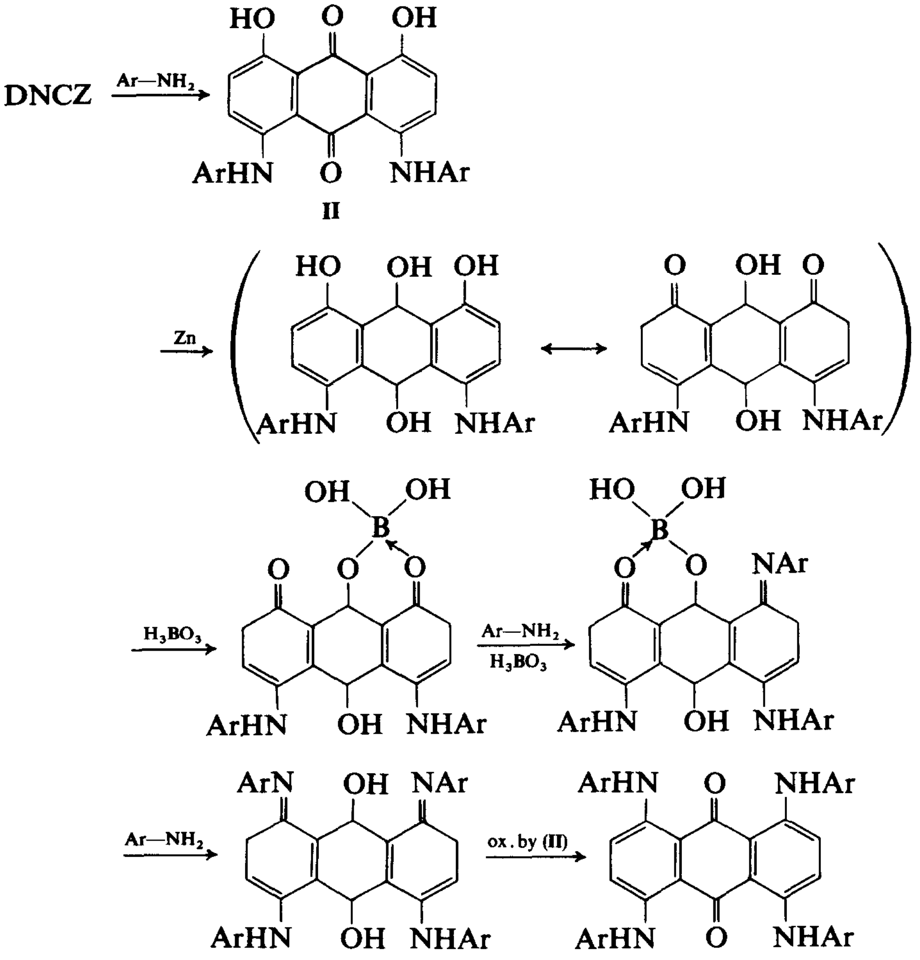
I

3 RESULTS AND DISCUSSION

3.1 Synthesis

The replacement of one hydroxy group in DNCZ with arylamines has been carried out in the presence of boric acid,[10–12] but the mechanism of this reaction has not been well described.

Shkal'kova and Barkov[13] have studied the function of boric acid in the reaction between quinizarin (and 1,4,5,8-tetrahydroxyanthraquinone) and arylamines in the presence of a reducing agent. They pointed out that the arylamination goes through the stages of boric esters, which react more

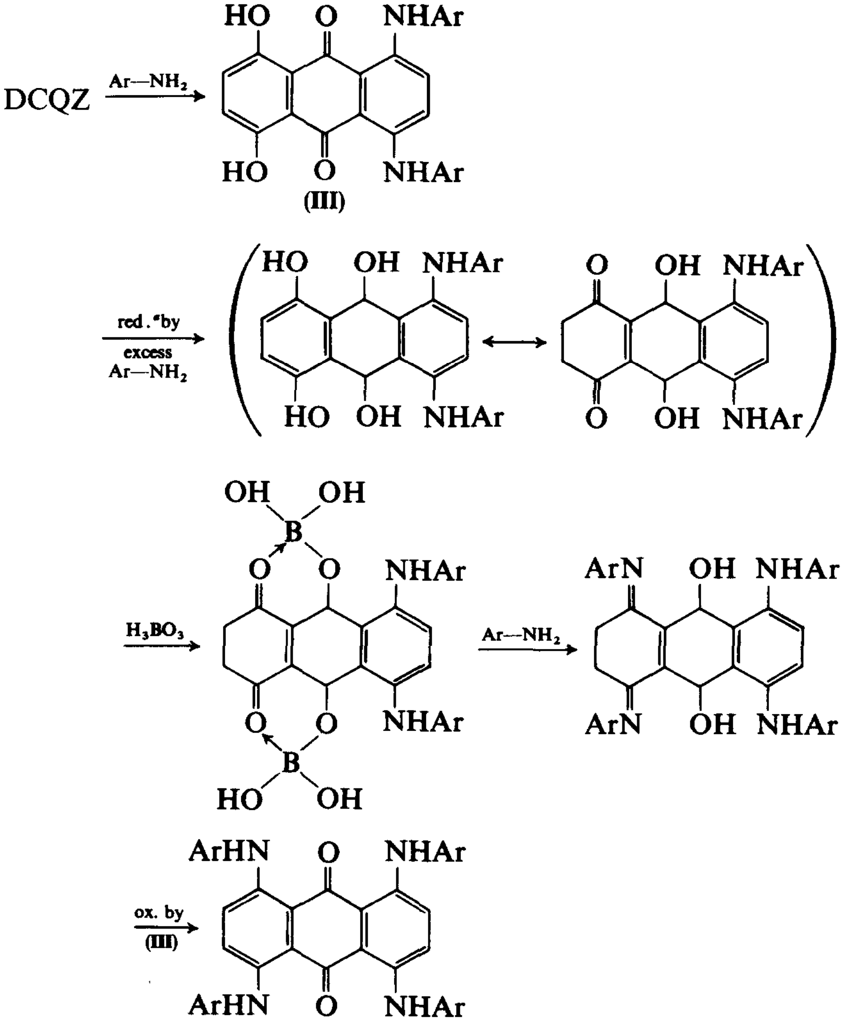


Scheme 1. For dye **I** (Method A).

readily with arylamines than the parent compounds. They also found that, under the arylamination conditions, quinizarin (and 1,4,5,8-tetrahydroxyanthaquinone) does not give an ester with boric acid, but that esters are readily obtained with leuco-quinizarin and leuco-tetrahydroxyanthraquinone.[13] Since quinizarin type compounds can have 'quinonoid' structures in the outer ring, they are especially reactive.[14]

In this present study, condensation of DNCZ with excess arylamine in the presence of boric acid and zinc powder gave 1,4,5,8-tetrakis(arylamino)-anthraquinones. These compounds were also obtained by condensation of DCQZ with excess arylamine in the presence of boric acid and potassium acetate.

Possible mechanisms are shown in Schemes 1 and 2.



Scheme 2. For dye I (Method B). ᵃTwo arylamino groups, neighbouring carbonyl groups, allow III to be easily reduced.

3.2 Electronic spectra

1,4,5,8-tetrasubstituted anthraquinones are among the most bathochromic of anthraquinone dyes because the major contributing structures to the excited states each contain a naphthalene ring.[15]

Replacement of the four amino groups in 1,4,5,8-tetrakis(amino)anthraquinone[16,17] (λ_{max} 600 and 629 nm in MeOH and λ_{max} 610 nm in CH_2Cl_2) by anilino groups results (dye **I.1**) in a large bathochromic shift of absorption maxima to 700 and 750 nm due to the additional conjugation influence of the aryl groups.

Introduction of the electron-donor ethoxy substituent into the phenyl rings gives further bathochromic shifts of 20 nm (dye **I.2**).

3.3 Dyeing and fastness properties

Both dyes give level green colouration on polybutylene terephthalate films. Fastness to light and sublimation was very good. The molar extinction coefficients (log ε) of near IR light (over 750 nm) of both dyes were higher than those of many anthraquinone derivatives and the width of the near IR absorption band of both dyes was very narrow (about 160 nm). Both dyes thus meet the requirements for use in optical data disks.

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